Carbon Sequestration Technology Roadmap and Program Plan 2006



Developing the Technology Base and Infrastructure to Enable Carbon Sequestration as a Greenhouse Gas Mitigation Option





Message to Our Stakeholders

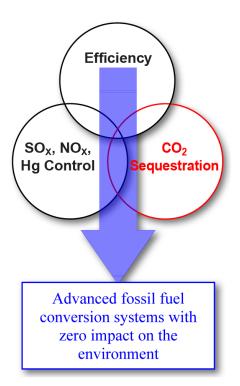
Carbon sequestration, the idea of capturing carbon dioxide before it is emitted to the atmosphere and storing it in underground rock formations or otherwise sequestering it, has progressed steadily over the past ten years. It is now poised to become a key technology option for greenhouse gas emissions abatement.

The U.S. Department of Energy (DOE) has taken a leadership role in the development of carbon sequestration technology through its Carbon Sequestration Program. The Program is managed within DOE's Office of Fossil Energy and implemented through the National Energy Technology Laboratory (NETL). The goal of the DOE program is:

"To develop by 2012 fossil fuel conversion systems that offer 90% CO₂ capture with 99% storage permanence at less than a 10% increase in the cost of energy services."

DOE's Carbon Sequestration Program is coordinated with efforts aimed at improving power plant efficiency and criteria pollutant control. Through these combined efforts, DOE seeks to develop coal-fired power plants and other fossil fuel energy systems that emit no criteria pollutants and put negligible strain on the global climate system — at the same cost as today's technology.

This document (1) defines the current status of carbon dioxide (CO_2) capture and sequestration technology, (2) identifies research pathways that lead to achievement of the Carbon Sequestration Program goal, and (3) describes efforts that the DOE program is pursuing along priority pathways.



The following are highlights from the Program activities over the past year:

- Regional Carbon Sequestration Partnerships. In 2005 the Regional Carbon Sequestration Partnerships progressed from an initial Characterization Phase to a Validation Phase. During the Validation Phase, the Regional Partnerships will conduct twenty-five field tests in which CO₂ will be injected into underground formations and its fate and transport monitored. The geologic settings span a range of geologic formations, and all tests include significant reservoir modeling components as well as testing of CO₂ detection and monitoring technologies. Together, these field tests will expand our understanding of the CO₂ storage option, facilitate more accurate estimates of CO₂ storage capacity, and establish a national infrastructure that may support future carbon sequestration deployments.
- Amine-based CO₂ Capture. Pilot-scale tests and modeling efforts show that operating an amine stripper at a vacuum can provide a 5-10% reduction in energy use per unit of CO₂ captured. This reduction is below the current state of the art of 1,400 Btu/lb and takes into account the extra CO₂ compression cost associated with operating the stripper at a vacuum.

• Novel CO₂ Capture Technologies.

- Novel Metal Organic Frameworks (MOFs) show great promise as CO₂ sorbents. In particular, MOF 177 can adsorb 1.4 grams of CO₂ per gram of sorbent material (at 600 psi). As a comparison, one gram of commercially available zeolite adsorbent can hold approximately 0.3 grams of CO₂. A higher storage capacity can lower the size and cost of a CO₂ capture system.
- A new type of organic salt, an ionic liquid, has shown a CO₂ dissolution capacity of 5 wt%. This is an improvement compared to 3 wt% for Selexol, and unlike Selexol, ionic liquids are stable at warm gas temperatures (450 °C) enabling more energy efficient CO₂ capture from an oxygen-fed gasification process.
- Stacked Geologic Formations. Researchers have pioneered the concept of a geologic sequestration field test using "stacked formations." In this approach, a CO₂ injection test is conducted in a saline formation that underlies a depleting oil or gas formation. The oil or gas formation's proven seal offers a second containment barrier against CO₂ migration beyond the saline formation cap rock. The stacked setting facilitates the use of a single injection well for two sets of experiments and expedites experimentation with saline formations, which are not as well understood as oil and gas bearing formations. Several of the field tests being conducted under the Regional Partnerships effort have adopted this approach to CO₂ sequestration.

Interaction with private and public sector stakeholders is critical to the success of the Carbon Sequestration Program. DOE engages stakeholders through cost-shared R&D projects and through the Regional Carbon Sequestration Partnerships. Stakeholders also interact with the Program via the Annual Conference on Carbon Sequestration, the Annual Project Review Meeting, and the National Environmental Policy Act (NEPA) process. The Program seeks to proactively raise awareness and understanding of carbon sequestration via a variety of methods, including the participation of DOE/NETL managers in conferences and meetings, the DOE Fossil Energy (FE) and NETL web pages, the monthly Carbon Sequestration Newsletter, and the development of various informational materials including educational curricula designed for middle school and high school students.

This document is itself an important medium for engaging stakeholders. We invite interested readers to examine it carefully and provide feedback to the contact persons listed on the inside back cover.

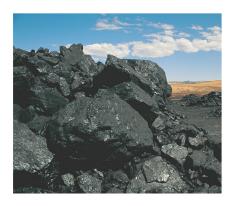






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GLOBAL CLIMATE CHANGE

Emissions of carbon dioxide (CO₂) from human activity have increased from an insignificant level two centuries ago to over twenty five billion tons worldwide today (Figure 1). Emissions of non-CO₂ greenhouse gases (methane, nitrous oxides, and fluorocarbon refrigerants) increased the total to over 30 billion tons CO₂ equivalent in 2004.

The greenhouse gas effect, the trapping of heat within the atmosphere by various greenhouse gases (GHGs), is a natural and important phenomenon for the earth's ecosystem. However, the additional GHGs in the atmosphere have significantly increased above the pre-industrial level. This increase of GHGs is considered by many to contribute to the phenomenon of global warming and could cause unwelcome shifts in regional climates.

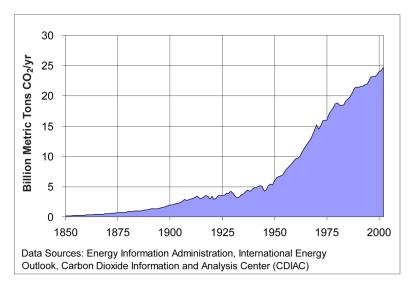


Figure 1. Worldwide CO₂ Emissions from Fossil Fuel Combustion and Cement Manufacture

The United States and 101 other countries are signatories to United Nations Framework Convention on Climate Change (UNFCC), a treaty which calls for stabilization of atmospheric GHGs. Business-as-usual forecasts, however, predict a steady increase in GHG emissions from human activity over the next 100 years. Such projections are based fundamentally on a growing global economy and abundant fossil fuel resources (Figure 2 and Table 1). Many policy makers and energy industry professionals regard it as unlikely that accessible fossil fuel resources will be left unused, irrespective of the climate signal. This is especially true in developing nations with significant fossil fuel resources.

Conservation, renewable energy, and improvements in the efficiency of power plants, automobiles, appliances, etc. are important first steps in any GHG emissions mitigation effort. But those approaches cannot deliver the level of emissions reduction needed to stabilize the concentrations of GHGs in the atmosphere – especially against a growing global demand for energy. Needed are transformational energy technologies that decouple energy use, economic prosperity, and GHG emissions.

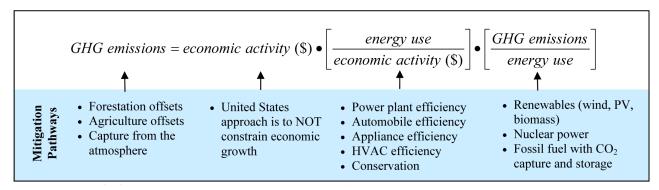


Figure 2. Greenhouse Gas Emissions Equation

Carbon sequestration, the capture and sequestration of CO_2 that would otherwise reach the atmosphere, offers the promise of a reasonable compromise – fossil fuel resources can be used but at a slightly higher processing cost in order to reduce net GHG emissions per unit of energy use by 80-100%. Carbon sequestration is a broad area encompassing many options. The CO_2 can be captured at the point of emissions or it can be removed from the air. The captured gas can be stored underground, absorbed by plants, or chemically converted to rock-like mineral carbonates or even back to hydrocarbon fuels.

There is a clear opportunity for carbon sequestration in the United States and the world under GHG emissions stabilization scenarios. Even in developed nations large numbers of new power plants and fuel processing facilities are expected to be built in the coming decades, creating ample opportunities for efficient and cost-effective CO₂ capture deployments. The United States in particular is underlain by large capacity geologic formations amenable to CO₂ storage.

		· -	
		Equiv	alent CO ₂
	Worldwide Resources	(billion metric tons CO ₂)	Equivalent atmospheric ppm*
Coal	1,000 B tons ^A	2,300	288
Crude Oil	2,300 B bbls ^B	1,000	125
Natural Gas	13,650 T scf ^B	700	87
Total		4.000	500

Table 1. Worldwide Fossil Fuel Resources and Equivalent CO₂ Emissions

Figure 3 sets forth a robust portfolio of sequestration field tests being conducted in the United States and worldwide. Sustained research is needed to reduce the cost of CO₂ capture and to better understand the permanence of CO₂ storage. The benefits of protecting the climate will be realized globally and far in the future, but the costs of each GHG emissions reduction project is local and immediate. Thus, there is a strong role for government in near term GHG mitigation technology development to ensure that the investment is at an optimum level for society. Beyond early niche opportunities, CO₂ capture and storage is strictly an added cost that relies solely on GHG mitigation benefits as a driver, further supporting a strong government role.

^A Recoverable coal reserves, Energy Information Administration – International Energy Outlook 2005

^B Includes remaining reserves, reserve growth, and undiscovered reserves, U.S. Geological Survey World Petroleum Assessment 2000; Proved reserves from EIA are 1,182 B bbls of oil and 6,436 T scf NG Does not include oil-bearing shales, methane hydrates, and other non-conventional supplies

^{*} Additional to the current level of 379 ppm, and net of any absorption by natural sinks.

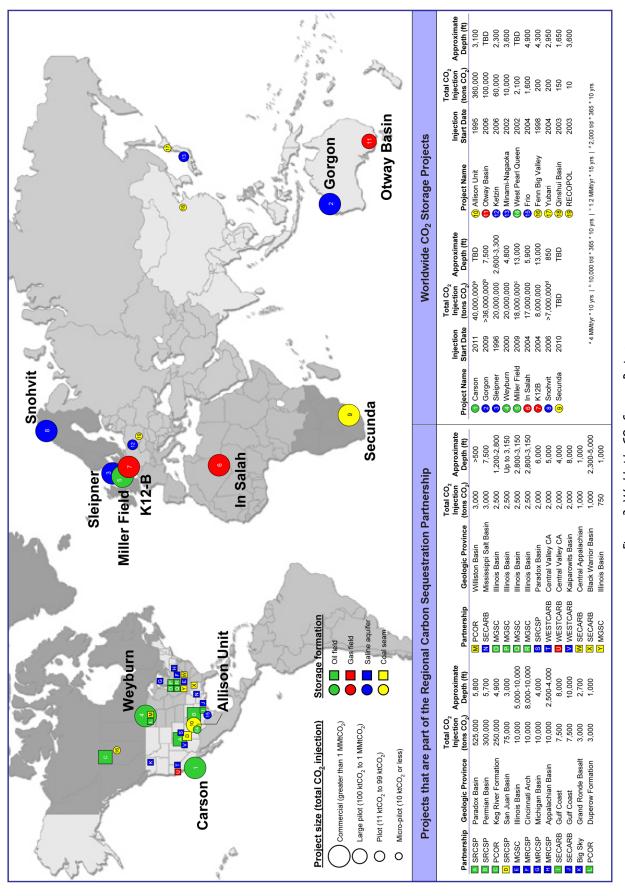


Figure 3. Worldwide CO_2 Storage Projects

THE DEPARTMENT OF ENERGY'S CARBON SEQUESTRATION PROGRAM

Figure 4 shows the elements of DOE's carbon sequestration technology development effort.

- A. Core R&D is the laboratory and pilot-scale research aimed at developing new technologies and new systems for GHG mitigation.
- **B.** Infrastructure is the groundwork for future carbon sequestration deployments being developed through the Regional Partnerships.
- **C.** Integration includes support for the FutureGen project, a DOE FE initiative to build the world's first integrated carbon sequestration and hydrogen production research power plant.

The Carbon Sequestration Leadership Forum (CSLF) is an international climate change initiative that is focused on the development of improved cost-effective technologies for the separation and capture of carbon dioxide for its transport and long-term safe storage. The purpose of the CSLF is to make these technologies broadly available internationally, and to identify and address wider issues relating to carbon capture and storage.

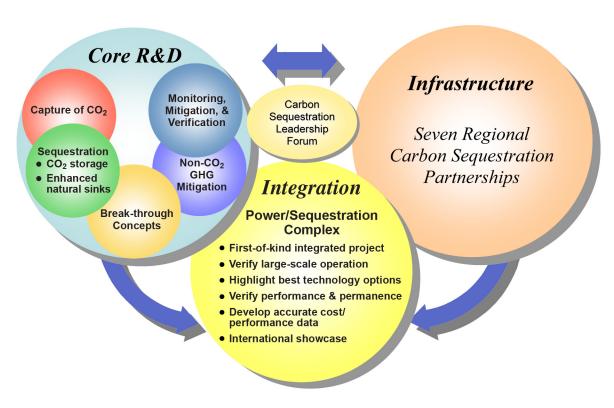


Figure 4. U.S. DOE's Carbon Sequestration Technology Development Efforts

This document describes in detail the Core R&D and Infrastructure elements, which are directly managed as a part of the NETL program. The Core R&D and Infrastructure efforts are aimed at achieving the program goal (Figures 5 and 6). Results from the core R&D program and the infrastructure development efforts will also contribute to the success of the CSLF and the FutureGen project.

90% CO_2 capture - the amount of captured CO_2 represents 90% of the carbon in the fuel fed to the power plant or other energy system.

Higher percent capture becomes incrementally more expensive as driving forces for separation decrease. 90% capture is deemed necessary to support "transformational" energy systems that can provide stabilization of GHG concentrations in the atmosphere. Development of options that offer less percent reduction, for example optimal-cost scrubbing (70-85%) or post-combustion adsorption (30-60%) is being led by industry and complements the DOE efforts.

99% storage permanence - after 100 years less than 1% of the injected CO₂ has leaked or is otherwise unaccounted for. Implied in this goal are advanced Monitoring, Mitigation, and Verification (MM&V) technologies and modeling capability that make it possible to prove 99% permanence. The goal is an average for all deployments. The test for success is whether projects can garner credits for 99% of injected CO₂.

90% CO2 capture with 99% storage permanence at

less than a 10% increase in the cost of energy services

by 2012.

10% increase in cost - this is a market-based goal. It is a level of cost increase that DOE deems will not adversely effect the economy or unduly effect U.S. competitiveness in international markets. It is also a level that is deemed necessary to enable fossil fuel systems with CO₂ capture and sequestration to compare favorably to nuclear power, wind, biomass, and other options to reduce the GHG intensity of energy supply. For the electricity supply sector the 10%-increase-in-cost target is based on plant gate cost from a newly constructed power plant with capital recovery. The cost of CO₂ capture and storage accounts for parasitic losses and includes CO₂ compression, pipeline transport of 50 miles, and injection into a saline formation. Revenues from CO₂ sales for EOR and ECBM are not credited against the cost of CO₂ capture. Net reductions in the cost of criteria pollutant control are included. The example on the facing page provides more detail on pathways to meet the goal.

By 2012 the program seeks to have pilotscale unit operation performance results from a combination of CO₂ capture, MM&V, and storage system components, such that, when integrated into a systems analysis framework, they would collectively meet the goal. Accounting for the lag associated with pre-commercial-scale validation and design and construction of commercial scale systems, projects that meet the program goal will result in commercial-scale units that come on line around 2020.

Figure 5. Anatomy of the Carbon Sequestration Program Goal

The Figure below shows an analysis of CO₂ capture technology performance applied to a coal fired power plant, and what is required to meet the program goal. The left column is a reference case no-capture power plant with technology that is projected to be online in 2020. This implies that the base power plant technology has been validated at the pre-commercial scale by 2015. The estimated efficiency and capital cost (47.4%, \$1,350 \$/kW) represent an improvement over current technology but do not include expected advancements from future government investments in base power plant research.

The right column is a power plant with 90% CO_2 capture. The estimated performance of both the base power plant and CO_2 capture system assume continued government investment in R&D. The lower cost and improved efficiency of the base power plant (52%, 1,100 \$/kW) lower its cost-of-electricity (COE) compared to the reference case scenario and "make room" for CO_2 capture; this base power plant improvement is due to government R&D investments. The box to the right presents one combination of capital and operating expenses for a CO_2 capture, transport, and injection system that provide a 10% increase in COE. Different capture technologies may offer trade-offs and provide different combinations of performance metrics that can achieve the goal.

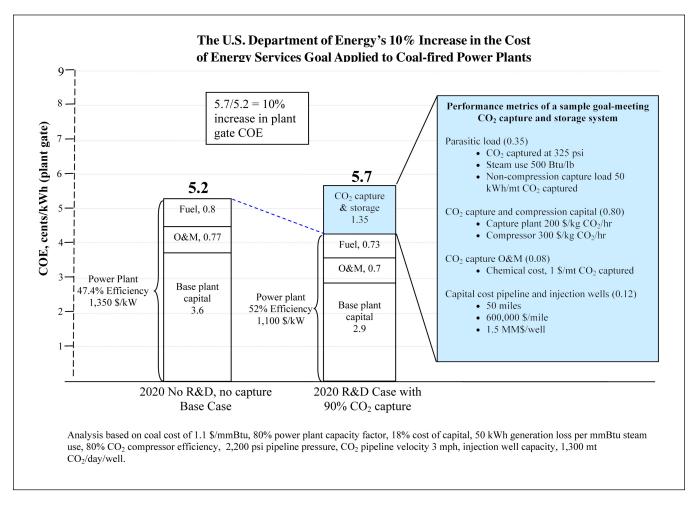


Figure 6. Meeting the Program Cost Goal

A. Core R&D

The Core R&D effort is a portfolio of work including cost-shared, industry-led technology development projects, research grants, and research conducted in-house at NETL. This effort encompasses the following five areas:

- I. CO₂ Capture
- 2. Carbon Storage
- 3. Monitoring, Mitigation, and Verification (MM&V)
- 4. Non-CO₂ Greenhouse Gas Control
- 5. Breakthrough Concepts

The first three Core R&D research areas track the life cycle of a carbon sequestration system. That is, first CO₂ is captured, then it is stored or converted to a benign or useful carbon-based product, and finally it is monitored to ensure it remains sequestered with appropriate mitigation actions to be taken if necessary. The fourth category, non-CO₂ greenhouse gas control, involves primarily the capture and reuse of methane emissions from energy production and conversion systems. The fifth area, breakthrough concepts, is a group of projects similar to the first four research areas, but with a higher technical uncertainty and the potential to expand the applicability of carbon sequestration beyond conventional point source emissions.

All research being conducted by the Carbon Sequestration Program is highlighted in the Carbon Sequestration Project Portfolio. To access the Project Portfolio, visit the NETL website www.netl.doe.gov From the sidebar at left, select "Technologies," and then "Carbon Sequestration." In the right sidebar, under "Publications & Projects," select "Carbon Sequestration Project Portfolio."

Table 2 is a top-level sequestration roadmap. It shows major pathways in each of the program areas, metrics for success that lead to the overall program goal, and highlights from 2006 in each area that show progress toward the metrics.

I. CO₂ Capture

The DOE CO₂ capture effort seeks to transform the fossil-based portion of the United States energy system from its current configuration to one in which CO₂ can be captured safely and cost-effectively. Efforts to develop technologies to capture or separate CO₂ from a process stream are being undertaken in concert with efforts to develop advanced, highly-efficient fossil fuel conversion processes.

Figure 7 shows three fundamental fuel conversion platforms. From the perspective of CO_2 capture, the three platforms offer different CO_2 partial pressures, different operating temperatures, and different components in the CO_2 -rich stream. Capture technologies are being developed to fit into one or more fossil fuel conversion systems.

Post-Combustion. Fuel is burned with air in a boiler to produce steam; the steam drives a turbine to generate electricity. The boiler exhaust, flue gas, is a combination of mostly nitrogen and carbon dioxide. To capture CO₂ from flue gas is a technical challenge because CO₂ is dilute (3-15 vol %), at low-pressure (15-25 psi), and for coal-based systems contaminated with traces of sulfur and particulate matter. However, air combustion is an important application because over 98% of existing power plants use air combustion technology and, as such, there is a strong degree of comfort with it within the United States electricity supply industry.

Table 2. Top-Level Carbon Sequestration Roadmap

	Dothwara	Metrics fo	Metrics for Success	2006 Status,
_	Гаштауз	2007	2012	Progress thus Far
CO2 Capture	Post-combustionPre-combustionOxy-fuel	Develop two capture technologies that result an increase in cost of energy services equal to no more than: • 20% for pre-combustion • 45% for post-combustion	Develop two capture technologies that result an increase in cost of energy services equal to no more than: • 10% for pre-combustion • 20% for post-combustion	 Operating an amine stripper at a vacuum can provide a 5-10% reduction in energy use per unit of CO₂ captured A regenerable sodium bicarbonate sorbent shows potential to achieve 20% increase in COE in post-combustion. A ceramic membrane that feeds pure oxygen directly to a fuel combustion zone shows reliable operation and an oxygen flux equal to 40% of target to achieve 10% increase in COE.
Sequestration/ Storage	Oil and gas bearing geologic formations Unmineable coal seams Saline formations Basalt formations Organic-rich shale Mineland closure/reclamation Ocean sequestration	Field tests provide improved understanding of the factors affecting permanence and capacity in a broad range of CO ₂ storage formations.	Demonstrate enhanced CO ₂ trapping and storage capacity at pre-commercial scale. Demonstrate ability to predict CO ₂ storage capacity with +/-30% accuracy.	 4D seismic, vertical seismic profiles, and other MM&V results from CO, injection sites have been used to improve models that estimate CO, capacity A fingering mechanism has been shown to increase brine mixing in CO, storage formation, thus enhancing CO, dissolution and storage permanence over long time frames. Hybrid poplars have been shown to grow well in reclaimed mineland.
Monitoring, Mitigation, &Verification (MM&V)	Detection and measurement of CO ₂ in geologic formations Fate and transport models for CO ₂ in geologic formations Remote sensing of aboveground CO ₂ storage and leaks Advanced soil carbon measurement	Demonstrate advanced CO ₂ measurement and detection technologies at sequestration field tests and commercial deployments.	CO ₂ material balance greater than 99%. M&&V protocols enable 99% of stored CO ₂ to be credited as net emissions reduction.	 Cross well seismic systems at Weyburn showed an ability to "see" CO₂ in an underground formation at a resolution of 2,500 tons CO₂. Sea floor gravity experiments conducted at Sleipner confirm seismic-based CO₂ plume tracking results. A method for measuring carbon stored in forests using multiple cameras and lasers attached to an airplane shows 95% correlation with results from traditional bushwhacking and trunk diameter measurement.
Breakthrough Concepts	 Advanced CO₂ capture Advanced subsurface technologies Advanced geochemical sequestration Novel niches 	Laboratory scale results from 1-2 current projects show promise to reach the goal of a 10% or less increase in the cost of energy, and are advanced to the pilot scale.	Technology from the program's portfolio revolutionizes the possibilities for CO ₂ capture, storage, or conversion.	 A novel CO₂ sorbent material, metal organic framework 177, can absorb 1.4 grams of CO₂ per gram of sorbent material (at 600 psi) – 4x the capacity of zeolite. An ionic liquid, (CF₃SO₂)₂N, has shown a CO₂ dissolution capacity of 5 wt% and stability at warm gas temperatures, both improvements over Selexol.
Non-CO ₂ GHGs	Minemouth ventilationLandfill gas recovery	Deployment of cost-effective methane capture systems.	Commercial deployment of at least two technologies from the R&D program.	A temperature-swing adsorption system based on advanced heat exchange technology shows the potential to separate nitrogen from methane cost-effectively.
Infrastructure Development	Geologic field tests Sequestration atlases Regulatory compliance Outreach and education	Priority sequestration opportunities are identified and field tests are initiated.	Results from the deployment phase projects enable and enhance commercial-scale carbon sequestration projects.	 Twenty-five field tests of CO₂ storage in geologic formations are planned or underway. Ten field tests of terrestrial sequestration are planned or underway.

Pre-Combustion. Fuel is converted into gaseous components by applying heat under pressure in the presence of steam. In a gasification reactor, the amount of air or oxygen available inside the gasifier is carefully controlled so that only a portion of the fuel burns completely. This "partial oxidation" process provides the heat necessary to chemically decompose the fuel, setting into motion chemical reactions that produce synthesis gas (syngas). Syngas is composed of hydrogen (H₂), carbon monoxide (CO) and other gaseous constituents. The CO in the syngas can react with steam to form CO₂ and additional hydrogen, leaving a stream of approximately 40% CO₂ and 60% H₂. Gasifiers can produce syngas at pressures as high as 950 psi, which combined with CO₂ provides a strong driving force for CO₂ separation at a very low cost. Syngas can be charged to a combined cycle power plant or used as a chemical feedstock.

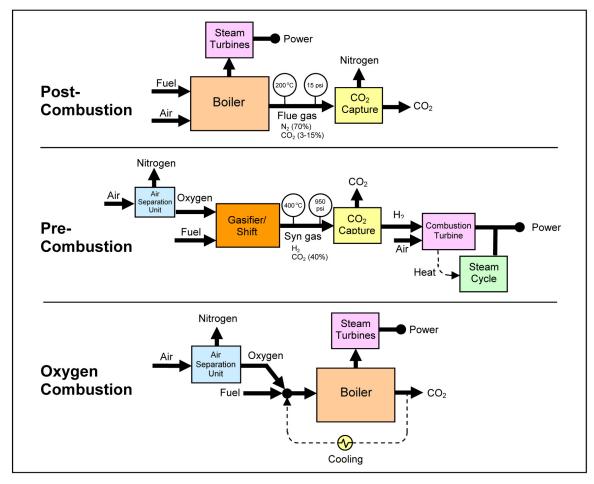


Figure 7. Fossil Fuel Conversion Platform and CO₂ Capture

Oxygen Combustion (oxycombustion). Fuel is burned in oxygen to produce steam to drive a turbine. This results in an exhaust of CO_2 and water vapor. Without nitrogen as a diluent, a portion of the CO_2 exhaust must be cooled and recycled to maintain the temperature in the combustion chamber within the limits of materials of construction. The economics of oxygen combustion are limited because it consumes roughly three times more oxygen per kilowatt-hour (kWh) than gasification.

There are a number of industrial processes that produce a highly pure stream of CO_2 as a natural consequence of their operation. These " CO_2 vents" include natural gas processing, ethanol production, and cement manufacturing. CO_2 vents represent less than 2% of total anthropogenic CO_2 emissions. NETL recognizes CO_2 vents as a near-term opportunity for CO_2 storage deployments, but seeks to develop technologies that can be broadly applied to fossil fuel based energy systems in the electricity supply and transportation sectors.

Figure 8 is a technology roadmap for CO₂ capture. It presents a range of technology development avenues that lead to the overarching program goal. The roadmap shows both advanced fossil fuel conversion and CO₂ capture technologies, recognizing the strong synergy between the two. Some of the pathways are being pursued in the private sector or by other entities within DOE. Those efforts complement the portfolio of capture research projects funded within the Carbon Sequestration Program.

Amines and Selexol (glycol) are two leading technologies in the area of CO₂ capture. Both are offered commercially, but have not yet been deployed at the scale being considered for CO₂ capture from power plants. Industry leads an effort to achieve incremental improvements in commercially offered amine and glycol technologies.

A range of other options for capturing and separating CO_2 offer the potential for a step change reduction in the cost and energy needed for CO_2 capture. DOE is funding a portfolio of cost-shared projects with industry, grants to research and academic institutions, and research conducted in-house at NETL, all aimed at developing these emerging options.

Table 3 presents more detailed information on selected CO_2 capture research pathways. In the left column is the pathway title, its level of maturity (commercially available, pilot scale, laboratory scale, or conceptual), and a list of key academic and private sector entities involved in the area. The next column presents advantages that the concept has demonstrated compared to established technologies, or ways in which it can enhance established technologies. The next column discusses trade-offs or disadvantages that the concept has compared to existing technologies. Finally, the right column lists priority research areas aimed at addressing the challenges and proving the advantages.

The portfolio of technologies being developed applies to both newly built systems and also retrofits of existing capital stock. Higher overall efficiencies and a lower cost of CO₂ capture can be achieved with new construction, but retrofits have the practical advantage of utilizing existing equipment.

Figure 8 sets forth a robust portfolio of research in the area of CO₂ capture. A number of different approaches, with different degrees of technology risk, are being actively pursued.

Metal Organic Frameworks

Scientists have recently developed improved capabilities to synthesize a class of chemical compounds called metal organic frameworks (MOFs) and "tune" their macromolecular properties. In a project funded by the Program, a team of researchers at UOP LLC, the University of Michigan, and Northwestern University are studying MOFs and their potential for CO₂ adsorption. Researchers are measuring the CO₂ adsorption isotherms of a set of MOFs with the hope of developing a better understanding of what MOF characteristics affect CO₂ adsorption. In early work MOF 177 (Zn₃O(BTB)₂) exhibited

a volumetric CO_2 sorption capacity 1.4 grams CO_2 per gram of sorbent material. This is an improvement over commercially available zeolite sorbents. The increased storage capacity can lower the size and cost of a CO_2 capture system.

MOF 177, Yaghi et. al Nature 427, 523-527 (2004)

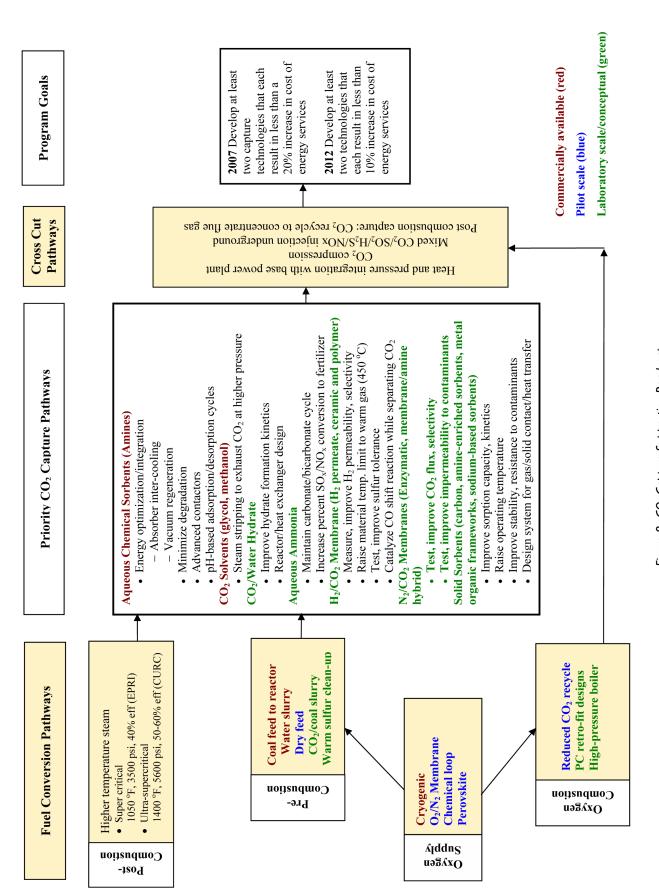


Figure 8. CO₂ Capture Supporting Roadmap

Table 3. ${\it CO}_2$ Capture and Sequestration Technology Pathways

	Description	Advantages	Challenges	R&D pathways
Amines Status: Commercially available Major suppliers: Fluor Mitsubishi Kerr/McGee	Amines undergo a chemical reaction with CO ₂ forming water soluble salts. In a conventional amine process an aqueous solution containing 25-30 wt% amine is contacted with flue gas or other CO ₂ -containing stream. CO ₂ in the vapor phase dissolves in solution and reacts with the amine to form a salt. The "rich" solution from the contactor is heated, causing the salts to disassociate. Stripping steam is used to pull CO ₂ from solution and recover it as a gas.	The amine/CO ₂ reaction is fast and enables aqueous amines to effectively scrub CO ₂ from post combustion flue gas where CO ₂ is dilute and at low pressure.	 Because amine sorption involves a chemical reaction, a significant amount of heat must be applied to recover the absorbed CO₂ (MEA, monoethanolamine, AH_R 825 Btu/lb CO₂ captured). Amine solution that is too concentrated, too rich, or too lean is corrosive to carbon steel. This effect is exacerbated by oxygen in flue gas which degrades corrosion inhibitors. Typical conditions (30 wt% amine, 0.45 mole CO₂ per mole amine rich, 0.20 moles CO₂ per mole amine lean) require 20 kg of water heated and cooled per kg of CO₂ absorbed. SO_x in the flue gas reacts with amines in solution to form heat stable salts. This causes amine attrition and also fouls heat transfer equipment. 	Scrubbing tower designs to reduce pressure drop (contact materials, intercooling) Additives that enable greater loading differential between rich and lean amine Heat integration with compression and power islands to reduce net steam load Vacuum regeneration
Glycol Status: Commercially available Major suppliers: UOP	CO_2 dissolves in a glycol solution.	CO ₂ recovery does not require heat to reverse a chemical reaction. CO ₂ and H ₂ S capture can be combined.	 Must cool down synthesis gas for glycol treatment and then heat back up again and rehumidify for firing to turbine. Low carrying capacity requires circulating 20+kg glycol solution per kg CO₂ captured. CO₂ pressure is lost during flash recovery. Some H₂ is lost with the CO₂. 	Systems concepts in which CO ₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure Systems concepts to reduce H ₂ loss
Methanol Status: Commercially available (Rectisol) Major suppliers: Lurgi	CO_2 -rich stream is cooled and contacted with liquid methanol. The methanol readily dissolves the CO_2 .	• Capable of CO ₂ capture rate in excess of 90%; possible use as a polishing stage.	Refrigeration costs hurt the economics compared to glycol systems.	

Table 3. ${\rm CO_2}$ Capture and Sequestration Technology Pathways (cont.)

	Description	Advantages	Challenges	R&D pathways
Aqueous Ammonia	Ammonia reacts with CO ₂ to form	Reduced heat of reaction	• Need to cool down flue gas to 80 °F for	Process optimization to
Status: Laboratory scale	the ammonium carbonate disassociates releasing a pure stream of CO ₂ .	J NO _x rr by-product	 ammonia caroonate to be stable. Reaction cycles involving ammonia reacting with CO₂ do not offer energy savings 	 Increase CO₂ loading Additives to raise process temperature above 70 °F
R&D by:		(ammonium sulfate and ammonium nitrate).	compared to amines. • Degradation of carbonate in the CO.	Increase percent conversion of SO, and NO, to fertilizer by-
Powerspan In-house NETL			absorber causes ammonia slip in the flue gas exhaust.	
Membrane/liquid sorbent hybrids	Flue gas is contacted with a membrane, and a sorbent solution on the permeate	The membrane shields the amine from the contaminants in flue	The membrane shields the amine • Capital cost associated with the membrane. from the contaminants in flue • Membranes may not keep out all unwanted	Pilot-scale tests
Status:	side absorbs CO ₂ and creates a partial pressure differential to draw CO ₂	gas – reducing attrition and allowing higher loading	contaminants. • Does not address CO; compression costs.	
Laboratory scale	across the membrane.	differentials between lean and		
$R\&D\ by$: Kvaerner/MHI				
Hydrogen / CO ₂ membranes	A membrane material selectively allows H, to permeate, leaving a	• Can deliver CO ₂ at high-pressure, greatly reducing compression	• Membrane separation of H_2 and CO_2 is more challenging than the difference in	• Measure, improve H ₂ bermeability, selectivity
	e	costs.		Operation temperature close to
Status: Laboratory-scale			 Due to decreasing partial pressure differentials, some H₂ will be lost with the 	warm gas (450 °C) • Sulfur tolerant materials
R&D h	transport hydrogen via diffusion or ion	• H ₂ permeation can drive the CO	CO ₂ . • Hydrogen commession is required which	Catalyze CO shift reaction at
R&D by. LANL	for gasification-based energy systems)	Ħ		Systems analysis to identify
Eltron ORNL		lower cost/higher temperatures.	pressure.	optimal places for membrane separation in an IGCC
NETL in-house				•
Metal Organic Frameworks	Large molecules with engineered macro-molecular cavities that can	ssible.	Unknown contaminant sensitivity. Unknown thermal, oxidative, and hydrolytic	Develop a better understanding of the adsorption process
Status:	adsorb CO _{2.}	required to recover CO _{2.}	stability.	Screen/design new MOFs
Laboratory scale				
R&D by: UOP; U of Mich; Northwestern U				
INDICITIVESICILI O.				

Table 3. ${\it CO_2}$ Capture and Sequestration Technology Pathways (cont.)

		-		
	Description	Advantages	Challenges	R&D pathways
Hydrates Status: Laboratory scale R&D by: Simtech LANL	At high pressure and low temperature (200 psi, 4 °C) CO ₂ and water form solid macromolecular structures called hydrates. The solids are separated from the liquid stream and then heated to break down the hydrates and recover CO ₂ .	• Has the potential to produce captured CO ₂ at several hundred psi of pressure.	• Requires refrigeration energy to counteract heat of hydrate formation (ΔH _F 600-1,400 Btu/lb CO ₂ captured). • Cold spots in the hydrate formation reactor can cause ice formation and operational problems.	 Additives to speed up the hydrate formation reaction and enable 90% CO₂ capture. Heat exchanger design to ensure uniform temperatures in the hydrate reactor.
Enzymatic CO ₂ Sorbents Status: Laboratory scale R&D by: Carbozyme CO2Source	Enzyme-based system achieves CO ₂ capture and release by mimicking mammalian respiratory mechanism.	 Fast kinetics lower system size and cost. Resistance to SO_x and NO_x. pH swing based operation offers potential to produce CO₂ above atmospheric pressure. 	 100 °F operating limit and exothermic CO₂ sorption reaction require cooling of flue gas. Entrained solids in flue gas from coal boilers mayblock membrane channels. Possible sensitivity to acid gases. 	Develop and test thermal management approaches Demonstrate insensitivity to SO _x , NO _x , and acid gas
Amine-enriched Sorbents Status: Laboratory scale R&D by: NETL in-house	A carbon material with amine compounds fixed upon it exposed to a CO_2 -rich process stream. The amine sites absorb the CO_2 . The temperature of the material is raised to release the CO_2 .	 High storage capacity (4 moles CO₂ per kg solid sorbent) and use of tertiary amines allows potential for lower energy required per CO₂ captured. 	Relative to a liquid, it is difficult to lower and raise the temperature of a solid material – can cause slow de-sorption rates. Small diameter particles can cause high pressure drop across absorber.	 Improve sorption capacity, kinetics Improve stability, resistance to poisons System design for gas/solid contact/heat transfer Multi-pollutant capture
Ionic liquids Status: Laboratory scale R&D by: U. of Notre Dame Sachem; Merck	lonic liquids are a broad category of organic chemical compounds consisting of anionic and cationic components. They can dissolve gaseous CO ₂ and are stable at temperatures up to several hundred degrees C.	 In a gasification application, can avoid cooling down syngas and heating it back up. Physical solvent requires little heat for CO₂ recovery. 	Room temperature ionic liquids are not manufactured commercially and are expensive (\$350 - \$2,000/kg). High viscosity may hinder usefulness.	 Develop better understanding of CO₂ dissolution mechanism Screen materials for CO₂ solubility, viscosity, thermal stability Conduct toxicity tests

Systems Analyses for CO₂ Capture Technologies

Systems analyses and economic modeling of potential new processes are crucial to providing sound guidance to R&D efforts. Analyses conducted under the auspices of the Program are focused on CO₂ capture technologies. Analyses are being performed on NETL in-house projects and also on processes being developed by universities and industry. Some of these studies, particularly on developed technologies, are performed by engineering firms and provide detailed, high-quality estimates. Other studies on emerging technologies that are being developed on a laboratory scale are less rigorous, because less information is available. Nevertheless, these less rigorous studies provide a vision of how a new technology might be applied to a full-scale power plant and identify potential issues with its integration. Figure 9 summarizes a recently completed analysis.

System analyses have multiple goals: (1) put emerging technologies into a systems context (e.g., commercialscale power plant), (2) screen out unpromising projects before significant resources are spent on them, and (3) provide guidance to NETL technology managers and researchers working on more promising projects.

In 2005, a Phase I systems analysis was completed on a CO₂ capture sorbent being developed at NETL. The sorbent uses the same type of amine chemicals (primary, secondary and tertiary) as found in conventional wet scrubbers, however, they are attached to solid substrates (meso-porous silica) rather than dissolved in water. This offers two primary advantages:

1. Uses less energy

- ↓ Heat Capacity (Do not need to heat water)
- Use less stripping steam to regenerate CO₂

	Amine Enhanced MEA Sorbents				
Heat Capacity (Btu/lb-°F)	(0.3	0.9		
∆T Regeneration	80°F		105°F		
Regeneration Energy (Btu/lb CO ₂)					
Sensible		40	941		
Reaction	+	580	703		
Vaporization	+	0	290		
Total	=	620	1,934		

2. Higher CO₂ carrying capacity per lb of sorbent

	30% MEA	Amine Sorbent
Density (lb/ft³)	22	44
Working Capacity (lb CO ₂ /lb sorbent)	0.052	0.264
Mass sorbent per pound CO ₂	19 lbs solution	3.8 lbs sorbent
Volume per Pound CO ₂ (ft³/lb CO ₂)	0.8	0.08

10x decrease in volume to treat equivalent amount of CO2 70% H₂O VS. 30% MEA

Conceptual designs of the solid sorbent in fixed and fluidized bed reactors were modeled by the NETL systems analysis group using ASPEN and EXCEL. The CO₂ capture systems were fully integrated into an air combustion power plant and sized to capture 90% of the CO₂ contained in boiler flue gas CO₂. The systems analysis revealed challenges in pressure drop across a fixed bed reactor and also in heat management issues. Fluidized-bed reactor designs showed promise in overcoming the pressure drop and heat management issues; but, at the expense of increased sorbent attrition rate. The analysis is currently investigating novel reactor designs that may alleviate the pressure drop and heat management issues. NETL is collaborating with Calgon Carbon Corporation to assess the feasibility of using their PhoenixTM radial flow reactor design for the solid CO₂ sorbent application.

Figure 9. Example: CO₂ Capture System Using Amine-Enriched Sorbents

2. Carbon Storage.

Carbon storage is defined as the placement of CO₂ into a repository in such a way that it will remain stored (or sequestered) permanently. It includes three distinct sub-areas: geologic sequestration, terrestrial sequestration, and ocean sequestration.

 CO_2 Storage in Geologic Formations. The storage of CO_2 in a geologic formation is the injection of CO_2 into an underground formation that has the capability to contain it securely over a long period of time. Five types of formations, each with different challenges and opportunities for CO_2 storage are:

- Oil and Gas Bearing Formations. An oil or gas formation is a formation of porous rock that has held crude oil or natural gas (both of which are buoyant underground like CO₂) over geologic timeframes. It thus has a "demonstrated seal" and is fundamentally an ideal setting for CO₂ storage. The attractiveness of oil and gas formations is often enhanced by the fact that injected CO₂ can enable the production of oil and gas resources left behind by primary recovery and water flooding. The challenge is that well-known oil and gas fields have been drilled into extensively. Earlier wells were not sealed to today's high standards when they were abandoned, and most abandoned wells, old and recent, are plugged with Portland cement which is susceptible to corrosion from saline water with dissolved CO₂.
- Saline Formations. A saline formation is a formation of porous rock that is overlain by one or more impermeable rock formations and thus has the potential to trap injected CO₂. Saline formations lack a demonstrated seal and do not offer the possibility for enhanced oil or gas production. The advantages of saline formations include a large aggregate CO₂ storage capacity and the low number of existing well penetrations compared to oil and gas formations.
- Basalts. Basalts are formations of solidified lava. They generally have low porosity; the CO₂ storage mechanism of interest in a basalt formation is mineralization of CO₂ with silicates. Research is focused on enhancing and harnessing the mineralization reaction and increasing CO₂ flow within a basalt formation.
- *Deep Coal Seams*. CO₂ injected into a coal bed becomes adsorbed onto the coal's surface and is sequestered. Most coals contain adsorbed methane, but will preferentially adsorb CO₂. CO₂ can be injected into an unmineable coal formation to enable recovery of residual methane not produced by de-pressuring. Research is focused on maintaining CO₂ injectivity as the coal adsorbs CO₂ and swells.
- Oil or Gas Rich Shales. Shale, the most common type of sedimentary rock, is characterized by thin horizontal layers of rock with very low permeability in the vertical direction. Many shales contain 1-2% organic material, and the hydrocarbon material provides an adsorption mechanism for CO₂ storage, similar to CO₂ storage in coal seams. Research is focused on achieving economically viable CO₂ injection rates, given the shales' low permeability.

Figure 10 presents a synopsis of carbon sequestration storage pathways and program goals for CO₂ storage in geologic formations.

The following is a discussion of four key topics on CO₂ storage in underground geologic formations.

• CO₂ Fluid Properties Underground. At the temperatures and pressures of most underground formations (100 to 150 °F, 2,000 to 3,000 psi) CO₂ exists as a supercritical fluid - it has a density near that of a liquid but a viscosity near that of a gas. Managing the state of CO₂, specifically keeping it supercritical in the pipeline, down the injection well, and in the target formation, is an important part of system design.

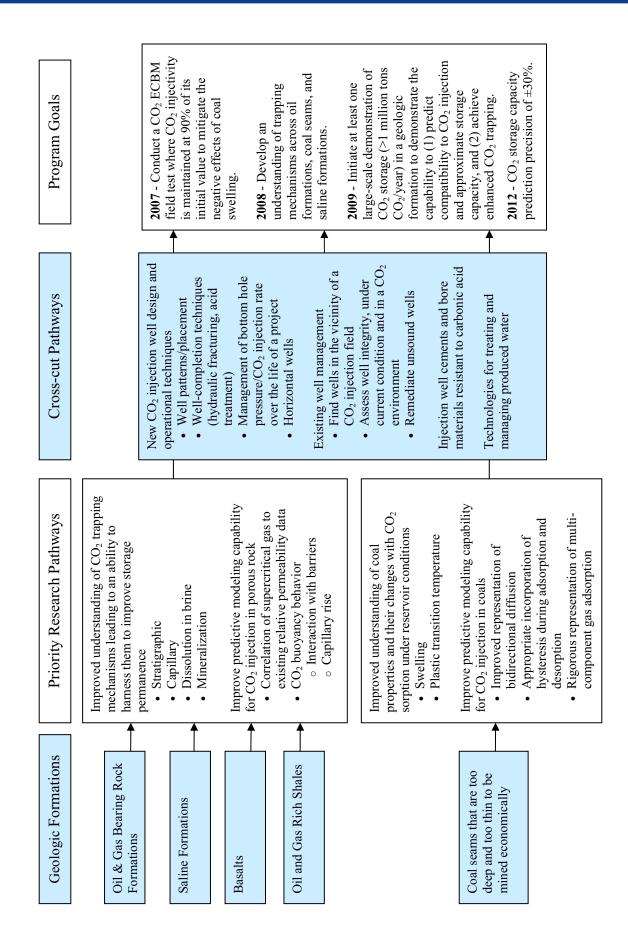


Figure 10. Carbon Storage Supporting Roadmap

- CO₂ Trapping Within a Geologic Formation. Of emerging importance in the field of geologic sequestration is the science of maximizing CO₂ trapping mechanisms (Figure 11). Supercritical CO₂ is lighter than the saline water in the formation and exhibits a strong tendency to flow upward. The primary method for trapping CO₂ is by a layer or "cap" of impermeable rock that overlies the formation of porous rock into which the CO₂ is injected and prevents upward flow of CO₂. This is called structural trapping and it is the mechanism that resulted in natural deposits of crude oil, natural gas and CO₂. Four other mechanisms for CO₂ trapping, described below, can enhance the permanence of CO₂ stored within a geologic formation.
 - 1. Capillary Trapping. The surface of sandstone and other rocks preferentially adheres to saline water over CO₂. If there is enough saline water within a pore (75-90% of the pore volume), it will form a capillary plug that traps the residual CO₂ within the pore space.
 - 2. *Dissolution in Saline Water.* CO₂ is soluble in saline water. As it comes in contact with the saline water it dissolves and forms a solution.
 - 3. *Mineralization*. Over longer periods of time (thousands of years), dissolved CO₂ reacts with minerals to form solid carbonates.
 - 4. Adsorption of CO₂. Coal and other organically-rich formations will preferentially adsorb CO₂ onto carbon surfaces as a function of formation pressure.

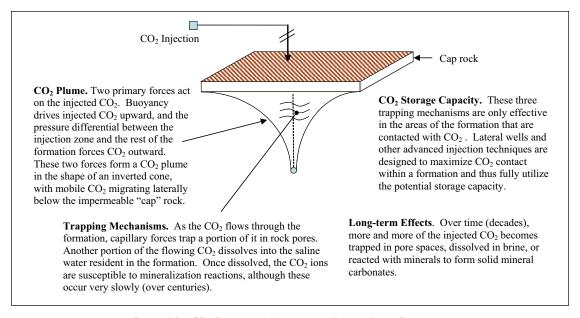


Figure 11. CO₂ Storage Mechanisms in Porous Rock Formation

- Produced Water. In many cases, storage of CO₂ in an underground formation will result in salty water (brine) being produced at the surface. Water is produced to control the pressure in the injection zone. Produced water can be pooled in shallow ponds and evaporated, or treated and utilized for irrigation. However, utilization of produced water requires cost prohibative desalination and treatment technologies, resulting in limited use.
- CO₂ Injection Wells. Proper engineering of injection wells is vitally important for the success of CO₂ storage projects. An optimal well will provide a high CO₂ injection rate and thorough contact between the injected CO₂ and the target formation. A well must also be stable and be able to withstand carbonic acid corrosion and, thus, not pose a risk as a potential leakage pathway. Figure 12 is a short primer on injection wells.

CO₂ Injection Wells – A Primer

The procedure for drilling a CO_2 injection well is as follows. A hole is drilled into the ground using a rotating bit. A drilling mud is circulated into the well bore to cool the drill bit and remove cuttings. A tubular metal casing is inserted into the well as the drilling proceeds.

After a certain distance a singular run of casing reaches its maximum length and drilling is paused. Wet cement or mud is pumped down into the well casing and pressured through the bottom of the well and up into the annulus between the casing and the well bore. When the mud sets, the casing is secured in place. If the target formation is deeper a smaller diameter hole is drilled below the first one with a new correspondingly smaller casing hung from the first one, and so on until the target formation is reached.

Diagnostics equipment is lowered into the well to verify the location and depth of the target formation. A shape charge is then lowered into the well and detonated at the target injection point. The charge perforates the liner and cement seal, allowing injected CO₂ to flow into the target formation.

A tube is lowered into the well. At the end of it is a cylindrical device called a plug. When the tube is in place, the plug expands forming a seal between itself and the outside of the tube and the inside of the casing. Injected CO₂ is pumped through the tube, and the tube wall provides another layer of protection against CO₂ leakage into a formation other than the target formation.

A pressure transient test is conducted. Water is pumped into the well to raise the bottom hole pressure. Then the flow of water is stopped, and the rate at which the bottom hole pressure dissipates is tracked. Too rapid a pressure dissipation indicates a fault in the seal between the liner and the well bore or a fault in the cap rock. Too slow a pressure dissipation indicates the permeability of the target formation may be insufficient.

CO₂ injection wells have some special considerations. For example, CO₂ must be dried thoroughly to minimize acid formation and the CO₂ injection pressure must be maintained to provide single-phase CO₂ in the well bore. Also, acid-resistant calcium phosphate-based cements may be used in place of the standard Portland cement which is susceptible to corrosion by brine with dissolved CO₂.

These technologies and procedures provide a sturdy and robust method for injecting ${\rm CO_2}$ into a target formation – without damaging the geologic seal. After injection is complete the wells are shut in by removing the tubing and filling the well bore with cement. The casing may also be pulled for its salvage value.

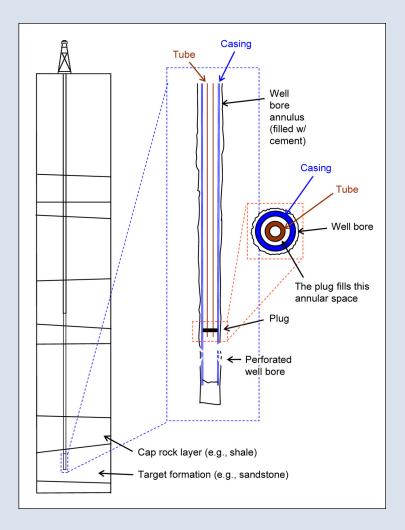


Figure 12. CO₂ Injection Wells – A Primer

Lateral wells are a relatively new development in well technology. Sedimentary formations are horizontal, and a lateral well can run along a formation, providing a much greater degree of contact compared to a conventional vertical well. For CO₂ storage, lateral wells create the opportunity of multiple injection points at the bottom of a formation, greatly increasing the lateral distribution of CO₂. Lateral well capability, combined with advanced formation characterization can enable placement of injection points that force CO₂ flow through low permeability regions, further expanding CO₂ storage capacity.

CO₂ Storage in Terrestrial Ecosystems. Terrestrial sequestration is the enhancement of CO₂ uptake by plants, both on land and in freshwater. It includes carbon storage in soils. Program efforts in the area of terrestrial sequestration are focused on increasing carbon uptake on mined lands. These activities complement research into forestation and agricultural practices that are being led by the U.S. Department of Agriculture (USDA). The U.S. DOE's Office of Science, the Environmental Protection Agency, and the Department of the Interior are also involved in terrestrial sequestration in supporting and complementary roles. Table 4 presents a synopsis of the terrestrial sequestration pathways and program goals.

With the passage of the Surface Mining Control and Reclamation Act of 1977 coal mine operators have moved away from reforestation of minelands in favor of compaction and grass planting. Afforestation provides more carbon sequestration per acre of land compared to grass planting, and the Program funded several field tests of afforestation methods. Tilling and amendment approaches developed by the Program provide a 6-10 foot layer of loose earth that enables trees to take root. In some cases the tilled mineland is amended with coal combustion by-products to reduce its acidity. A layer of compacted earth is maintained under the loose earth to prevent rain water from draining through the mine slag. These approaches can be applied to both closure practices at currently operating mines and reclamation of the nearly 1.5 million acres of lands in the United States damaged by past mining practices.

Table 4. Terrestrial and Ocean Sequestration Pathways and Program Goals

Te	chnology Roadmap		Supporting Progr	ram Activities
Current State of the Art	Priority Research Pathways	Cross Cut Pathways	R&D Highlights	Program Goals Ensure permanence and ecosystem protection
Terrestrial Sequestration There are currently over 20,000 acres of forestland in the United States dedicated specifically to sequestering CO ₂ . The United States has 1.5 million acres of land damaged by past mining practices.	Planting trees instead of grass on mine land Soil reclamation using coal combustion by-products (CCBs) or other solid residuals No-till farming, afforestation, and other activities applied to a wide range of geographies to increase carbon uptake	Enhanced carbon transfer from plant to soil	Achieved 80% survival rate for tree plantings in both damaged land amended with flue gas desulfurization sludge (Paradise, KY) and in formerly compacted mineland (Hazard, KY).	2007 - Develop optimization strategies and best practice guidelines for maximizing carbon sequestration potential on unproductive mine lands. 2008 - Develop to the point of commercial deployment systems for advanced indirect sequestration of greenhouse gases that protect human and ecosystem health and cost no more than \$10 per metric ton of carbon sequestered, net of any value-added benefits.
Ocean Sequestration No commercial deployments. Unknown ecosystem impacts. Enormous storage potential.	Ocean injection - Deep injection technology - Use of hydrates to increase permanence	Developing equipment needed to conduct experiments in the deep ocean	An experiment conducted at a natural CO ₂ vent in the ocean showed that fish can sense and avoid a plume of entrained CO ₂ . Laboratory tests have shown that premixing CO ₂ and water prior to injection creates hydrates that are denser than ocean water and sink upon injection.	Improved scientific understanding of this option. ***This portion of the program is being phased-out.

The results from field tests have been encouraging. Tree survival rates of greater than 80% have been achieved. Initial concerns about erosion before saplings become established have not been realized because the deep layer of loose soil soaks up the water.

 CO_2 Storage in the Ocean. Ocean sequestration is the injection of CO_2 into the deep oceans for long-term storage. Key concerns about such an approach include the cost of delivering CO_2 500 meters or deeper below the ocean surface, the permanence of injected CO_2 , and possible negative effects on the deep ocean ecosystem. The advantage of this approach is the enormous potential storage capacity of the deep oceans. Table 4 presents a synopsis of the ocean sequestration pathways and program goals.

In cooperation with U.S. DOE's Office of Science and the National Oceanic & Atmospheric Administration (NOAA) and the National Science Foundation (NSF), the Core R&D effort is funding research to assess the effects of injected CO₂ on aquatic organisms near the injection zone. A large part of the work has been devoted to prerequisite efforts of developing the instrumentation and remotely-operated-vehicles needed to conduct experiments in the deep ocean. Experiments have shown that some fish are able to detect and avoid a CO₂ plume. Other experiments have shown that sessile marine organisms contacted by a CO₂ plume experience a high mortality rates. Further research efforts are focused on the boundary layer between the CO₂ plume and the surrounding ocean and in measuring the pH gradient from the injection point outward.

3. Monitoring, Mitigation, and Verification (MM&V)

Monitoring and Verification are defined as the capability to measure the amount of CO_2 stored at a specific sequestration site, monitor the site for leaks or other deterioration of storage integrity over time, and to verify that the CO_2 is stored in a way that is permanent and not harmful to the host ecosystem. Mitigation is the capability to respond to CO_2 leakage or ecological damage in the unlikely event that it should occur. MM&V is broken into two categories (1) geologic sequestration and (2) terrestrial sequestration. Research activities in both areas are closely coordinated with the associated work in carbon storage. In addition to ensuring effective and safe storage, MM&V provides information and feedback that is useful in improving and refining storage field practices.

Key topics in the areas of geologic and terrestrial sequestration MM&V are discussed below. Figure 13 shows goals and research pathways.

MM&V Technologies for CO₂ Storage in Geologic Formations

Monitoring and Verification. Monitoring and verification for geologic sequestration contains three components:

• Modeling. Modeling is simulating the forces that influence the behavior of CO₂ in a geologic formation. A model is an important tool needed to prove, with a high degree of confidence, that injected CO₂ will remain securely stored before injection is allowed to commence. The behavior of injected CO₂ is a complex phenomena. It involves the flow of CO₂ through heterogeneous rock; forces acting upon the flowing CO₂, including dissolution, capillary trapping, and chemical reactions; and the impact of the CO₂ plume and increased pressure on the formation cap rock. A model serves as a nexus of understanding and captures the interaction of different forces. The boundary of a robust CO₂ storage model is not limited to the target formation, but also includes paths that fugitive CO₂ may travel up to the surface. The Program seeks to acquire data needed to support models (i.e., chemical reaction kinetics, and two and three phase vapor/liquid equilibrium data at super critical conditions) and to develop integrated models that support the needs of field tests.

- Plume tracking. Plume tracking is the ability to "see" the injected CO₂ and its behavior. Seismic is a key technology in this area. Supercritical CO₂ is more compressible than saline water and sound waves travel through it at a different velocity. Thus free CO₂ in a saline formation leaves a bright seismic signature, as seen at the Weyburn and Frio field tests. Observation wells are another important source of information for plume tracking.
- Leak detection. CO₂ leak detection systems will serve as a backstop for modeling and plume tracking. The first challenge for leak detection is the need to cover large areas. The CO₂ plume from an injection of 1 million tons of CO₂ per year in a deep saline formation for twenty years could be spread over a horizontal area of 15 square miles or more. The second challenge is to separate CO₂ leaks from varying fluxes of natural CO₂ respiration.

There are important interconnections among these three areas. For example, data from plume tracking enables validation of reservoir models. On the other hand, a robust reservoir model enables operators to better interpret data from plume tracking. Also, models and plume tracking help focus leak detection efforts on high-risk areas.

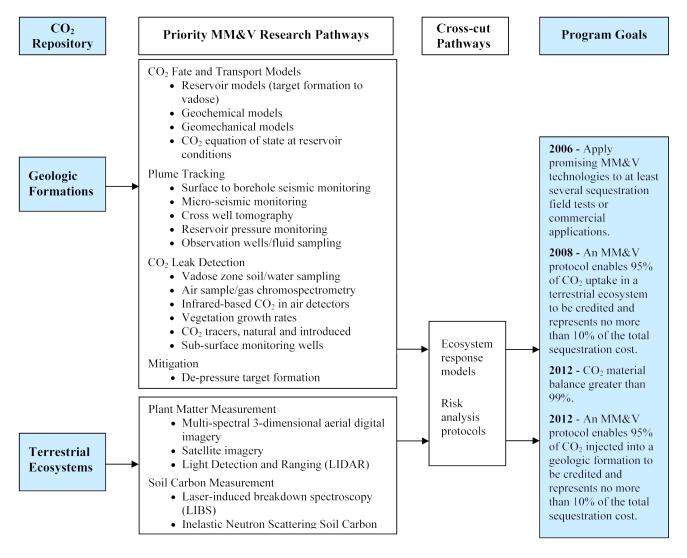


Figure 13. MM&V Supporting Roadmap

Mitigation. If CO₂ leakage occurs, steps can be taken to arrest the flow of CO₂ and mitigate the negative impacts. Examples include lowering the pressure within the CO₂ storage formation to reduce the driving force for CO₂ flow and possibly reverse faulting or fracturing; forming a "pressure plug" by increasing the pressure in the formation into which CO₂ is leaking; intercepting the CO₂ leakage path; or plugging the region where leakage is occurring with low permeability materials using, for example, "controlled mineral carbonation" or "controlled formation of biofilms."

MM&V for Terrestrial Ecosystems

Organic Matter Measurement. Researchers are developing video and laser-based fly-over technologies for estimating the amount of carbon stored in forests or other terrestrial ecosystems. Recent field tests of a video/laser measurement system showed a 95% correlation with results from traditional field measurements. The purpose of the fly-over and satellite technologies is to provide a less labor-intensive method for measuring stored carbon. Also, the advanced technologies can provide more robust information, which can enable more proactive forest management resulting in additional stored carbon.

Soil Carbon Measurement. The storage of carbon in degraded soils offers a significant opportunity to offset GHG emissions. The program is focusing its research on the development of advanced technologies to reduce the uncertainty and costs with measuring carbon in soils.

Modeling. Detailed models are used to extrapolate the results from random samples to an entire plot and to estimate the net increase in carbon storage relative to a case without enhanced carbon uptake. Economic models show accumulations of emissions credits and revenues versus an initial investment.

4. Non-CO₂ Greenhouse Gas Control

Because non- CO_2 greenhouse gases (e.g., methane, nitrous oxide, and certain refrigerants) can have significant economic value, emissions can often be captured or avoided at relatively low net cost. The Carbon Sequestration Program is focused on fugitive methane emissions where non- CO_2 greenhouse gas abatement is integrated with energy production, conversion, and use. Landfill gas and coal mine methane are two priority opportunities. Both opportunities have a lower-technology-risk pathway that involves combusting the produced methane and, thus, reducing the carbon's GHG effect by a factor of ten. Both also have a higher-technology-risk pathway that involves capturing the methane and utilizing it. Landfill gas is typically a 50/50 mixture of methane and CO_2 , with trace amounts of heavier hydrocarbons. Coal mine ventilation air methane (VAM) is much more dilute (0.3 - 1.5% methane in air) and represents a larger challenge. Table 5 presents a roadmap for non- CO_2 GHG control research and several supporting projects funded by the Program.

5. Breakthrough Concepts

Current technologies, commercially available and under development, hold the promise of lowering the cost of CO₂ capture and storage and achieving the Carbon Sequestration Program goal. However, DOE is still committed to fostering the innovative potential of industry and academia. The "breakthrough concepts" effort is an incubator for CO₂ capture, storage, and conversion concepts with the potential to provide step change improvements in energy use, complexity, and cost. A guiding principle for the breakthrough concepts effort is to mimic and harness processes found in nature, for example, photosynthesis and mollusk shell formation.

Table 5. Non-CO₂ GHG Roadmap

	Technology Pathway	Supporting Research Projects	Program Goals
Landfill Gas	Methane oxidation Bacterial tarp Methane/CO ₂ separation Use of landfill gas for ECBM Methane generation control Water management Microbe management	Methane recovery from landfills [Yolo County Planning and Public Works Department] Methodologies to minimize microbial production of nitrous oxide and maximize microbial consumption of methane in landfill cover soils [University of Michigan] Maximize biodegradation and minimize the formation of methane by controlled injection of air and liquids [University of Delaware] Design and test a landfill tarp impregnated with immobilized methane oxidizing bacteria [University of North Carolina] Injection of landfill gas into un-mineable coal seams [Kansas Geological Survey]	2007 - Effective deployment of cost-effective methane capture systems 2012 - Commercial deployment of at least two technologies from the R&D program
Coal Mine Methane	Methane oxidation Catalytic oxidation N ₂ /methane separation Thermal swing adsorption	Catalytic combustion of minemouth methane [Consol Energy] Nitrogen/methane separation via ultra-fast thermal swing adsorption [Velocys, Inc.]	

DOE has collaborated with the National Academies of Science (NAS) in the area of breakthrough concepts. A planning workshop identified priority areas of science and subsequent solicitation resulted in the eight awards shown in Table 6. The projects are showing progress and two, the metal organic frameworks (MOFs) and ionic liquids, are highlighted in the CO_2 capture section as promising pathways.

Table 6. Breakthrough Concepts Research Awards Through NAS/DOE Collaboration

Area	Title	Description
	Hydrogen Selective Silica Membrane	Develop a new method for making extremely thin, high-temperature, hydrogen-selective silica membranes. [University of Minnesota]
Advanced CO,	Dual Function Membrane	Develop a membrane that will use both pore structure and an amine chemical adhered to the membrane to achieve higher CO ₂ selectivity than is possible using pore size alone. [University of New Mexico, T3 Scientific]
Separation	Ionic Liquids	Conduct basic research into the use of ionic liquids (organic salts that are liquid at room temperature and exhibit unusual properties) for CO ₂ capture. [University of Notre Dame]
	Microporous Metal Organic Frameworks (MOFs)	Search for novel microporous metal organic frameworks (MOFs) suitable for CO ₂ capture. MOFs are hybrid organic/inorganic structures at the nano scale to which CO ₂ will stick. [UOP LLC, University of Michigan, Northwestern University]
	Carbonate Sediments Below the Sea Floor	Using laboratory-scale simulations, study the potential of calcium carbonate sediments to absorb injected CO ₂ at the elevated pressures and temperatures found in subsea formations. [Harvard University, Columbia University, Carnegie-Mellon University, University of California at Santa Cruz]
Advanced Subsurface Technologies	Mineral Dissolution Kinetics	Develop a better understanding of factors affecting silicate and dawsonite dissolution and the rate of CO ₂ mineralization in-situ. [University of Indiana, University of Minnesota]
	Mineral Carbonation	Study the chemistry and kinetics of the CO ₂ carbonation reaction in olivine and other commonly occurring minerals. Investigate the use of sonic frequencies and other methods to enhance the reaction. [Arizona State University]
Novel Niches	Microbial CO ₂ Conversion	Create strains of microbes that feed off CO ₂ and produce by-products, such as succinic, malic, and fumeric acids which can be used as food preservatives. [University of Georgia]

B. Infrastructure

The purpose of the Program's infrastructure effort is to develop, within the United States and Canada, the ability to accept and deploy the CO₂ capture and sequestration technologies being developed within the core R&D Program. Such an effort is deemed necessary by DOE so that organizations within the United States are prepared if future global climate change policies require large-scale deployments of sequestration technologies over a short period of time.

Different geographic regions of the country offer markedly different opportunities for carbon sequestration in underground formations. The range of possibilities include oil and gas formations, unmineable coal seams, saline formations, basalts, and hydrocarbon-rich shale. Among regions, formation types differ in their lithology, as well as in the locations of sinks relative to CO_2 emissions sources and pipelines. Some regions have an abundance of several different types of geologic sinks while in other regions opportunities are dominated by a specific sink. Opportunities for terrestrial sequestration are similarly varied. Given this diversity, DOE decided that a sequestration infrastructure development effort would need to be developed on a regional basis for sequestration opportunities.

DOE is pursuing infrastructure development via the Regional Carbon Sequestration Partnerships Program, which is funded and managed by NETL and implemented by entities located within various geographic regions. The Regional Partnerships approach is based on the belief that local organizations and people bring pertinent knowledge and experience to infrastructure development. In addition, local organizations function more effectively and efficiently than a centralized group. The Regional Partnerships' effort has three distinct phases:

- Characterization (2003-2005)
- Validation (2005-2009)
- Deployment (2009-2017)

By moving carbon sequestration technology from the laboratory to the field, we are another step closer to significantly reducing greenhouse gas emissions while maintaining the important role coal plays in America's energy mix.

Samuel Bodman U.S. Secretary of Energy June 2005

Characterization Phase (2003-2005)

The Characterization Phase began in 2003 with the selection of seven Regional Partnerships. Their efforts for this phase focused on characterizing regional opportunities for carbon capture and sequestration and identifying priority opportunities for field tests. Each of the Partnerships worked to develop decision support systems that housed the regional geologic data on sinks and information on sources to complete source-sink matching models. They also researched project tools that were necessary to model and measure the fate and transport of the CO₂ once it was injected. The Regional Partnerships participated in the Interstate Oil and Gas Compact Commissions working group to identify the necessary regulatory framework for implementing field validation tests, as well as the gaps in the current structure for implementing demonstration size sequestration tests. Finally, the partnerships worked to develop outreach and education programs to communicate the benefits and risks of carbon capture and storage to local communities.

As a result of the Characterization Phase, the seven Partnerships showed that carbon sequestration is a viable option to mitigate CO₂ emissions. In summary, Characterization Phase activities included:

- Identifying over 1,000 years of potential CO₂ storage capacity in the U.S. Coal seams, oil formations and gas formations hold a short-term opportunity that provides value added benefits spurring development. The long-term storage of CO₂ in saline formations will benefit from the fact that many of these very large formations underlie oil and gas resource recovery opportunity sinks.
- Identifying 126 trillion cubic feet of natural gas that could be recovered from coal seams and over 16 billion barrels of additional oil that could be recovered from depleting oil formations during sequestration operations.
 These benefits will help to offset the costs of developing the infrastructure necessary to transport CO₂ from sources to geologic sinks.
- Identifying terrestrial sequestration opportunities to offset CO₂ emissions through the reclamation of abandoned mine lands, modifying land management practices to increase soil carbon uptake, and reforestation of degraded lands, while applying the appropriate MM&V technologies to measure changes in carbon content. In addition, the Regional Partnerships developed project implementation guidelines, such as MM&V protocols and contracts, to take sequestration credits to future markets.

The Regional Partnerships have gathered and compiled information on CO₂ emissions point sources, geologic formations with sequestration potential, and terrestrial ecosystems with potential for enhanced carbon uptake – all referenced to their geographic location (longitude and latitude) for the purpose of matching sources and sinks.

Analytical tools were then developed through the Regional Partnerships in collaboration with the National Carbon Sequestration Database (NATCARB). These tools gave the Regional Partnerships the ability to evaluate the geology and terrestrial resources of the regions to identify potential sequestration opportunities. Tools have been developed to estimate storage capacity, estimate injectivity of CO_2 into geologic formations, match CO_2 sources with potential sinks, and estimate pipeline transportation costs for CO_2 . Layering the geologic information into a geographic information system (GIS) allowed the Regional Partnerships to assess the opportunity of CO_2 injection into stacked formations where oil, coal, and saline formations are at different depths.

Access to some of the analytical tools and all the data from the Characterization Phase is available through the NATCARB website (www.natcarb.org). NATCARB is a relational database management system with spatial query capabilities to evaluate the geographic distribution, physical characteristics, and economic parameters of potential CO_2 sources and geologic sequestration sites. NATCARB's mapping software enables a user to select a source and investigate sink or pipeline opportunities in the vicinity, in addition to many other features. The user can then calculate the potential storage capacity using the "sequestration buffer" feature, or use the "pipeline cost" feature to estimate the cost of constructing a pipeline. These are examples of the many features available through NATCARB and the individual Regional Partnerships systems. The suite of tools offered by NATCARB effectively allows users to match CO_2 sources to sinks. Efforts during the Validation Phase are aimed at filling in gaps in the data, updating information, and refining the database tools.

Validation Phase (2005-2009)

The Validation Phase began in 2005 and is focusing on the implementation of field tests to validate the efficacy of carbon sequestration technologies in a variety of geologic and terrestrial sinks throughout the U.S.. The seven Regional Partnerships identified the most promising opportunities for carbon sequestration in their regions during the Characterization Phase, and proposed a series of geologic and terrestrial field tests for the validation phase. The geologic tests are shown in Figure 14 and the terrestrial tests in Figure 15.

The first four projects listed in Figure 14 are larger, commercial-scale injections. These are all opportunities where a commercial partner is injecting CO_2 into geologic formations for the purposes of enhanced oil recovery and/or coalbed methane recovery. The Regional Partnerships are collaborating with industrial partners to provide additional reservoir modeling and MM&V. In the remaining tests the Regional Partnerships will inject a relatively small amount of CO_2 into coal seams, oil and gas formations, and saline formations. These tests will provide valuable insights into the suitability of these sinks as future sequestration sites. The major R&D issues these field projects will help to address are:

- Validate and refine the current CO₂ formation models for various sinks
- Collect physical data to confirm the capacity and injectivity estimates that were made during the Characterization Phase
- Demonstrate the effectiveness of MM&V technologies to measure CO₂ movement in the formations and the integrity of the seals
- Develop guidelines for well completion, operations, and abandonment to maximize storage potential and mitigate leakage
- Develop strategies for sequestration projects that can be used to optimize the storage capacity of the various sink types

As Figure 15 shows, the Regional Partnerships are pursuing a wide range of terrestrial projects consistent with varied ecosystems within the different regions. Several projects are focused on reclaiming damaged minelands and the use of produced water for irrigation and land remediation. Other projects are focusing on the reforestation of degraded lands and altering land management practices on rangelands and agricultural lands to increase soil carbon uptake. One project is looking to redevelop wetlands, which hold significant potential to store carbon and offset emissions of nitrous oxide. Some of the partnerships are working to develop the legal contracts and financial systems to aggregate a number of smaller projects to form an instrument that is large enough to trade in future CO₂ markets.

During the Validation Phase, the Regional Partnerships will continue their work on characterization of sequestration opportunities, maintenance of the regional GIS and DSS systems; researching permitting requirements for field projects with the IOGCC; and finally, taking steps to implement public outreach and education in the local communities where the field projects will be occurring to ensure that the issues related to the deployment of these technologies are well understood. Some examples of the diversity of approaches taken to involve the public in these efforts are listed in Table 7.

The Regional Partnerships are faced with numerous practical issues as the field tests begin. The tests have also drawn the attention of local entities and brought to light new perspectives on the issues associated with sequestration projects. To date, the field tests have been a positive learning experience for all involved and will help to define carbon sequestration's potential role as a technology option to mitigate GHG emissions.

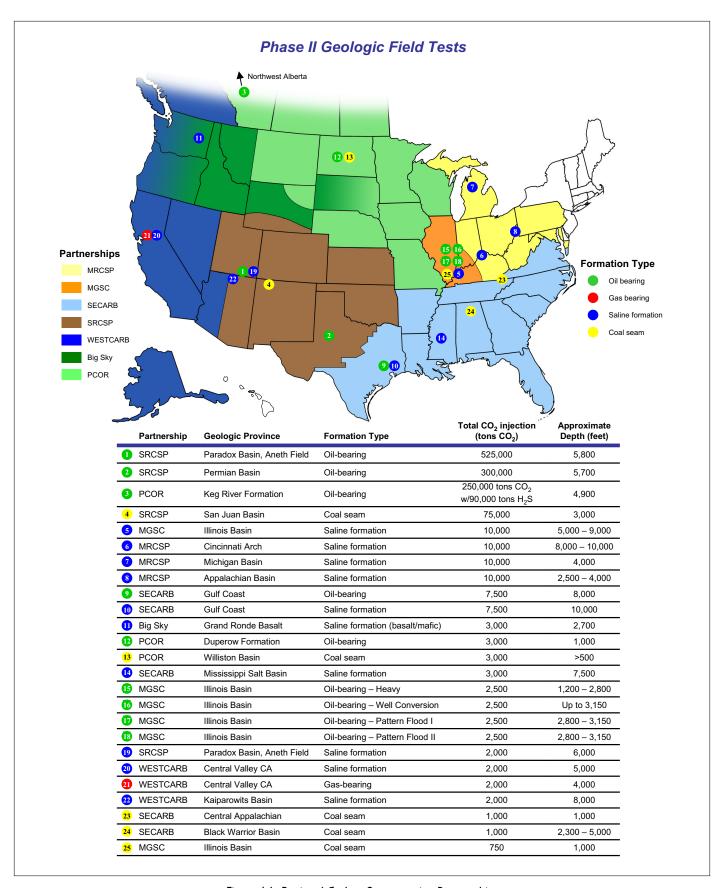


Figure 14. Regional Carbon Sequestration Partnerships

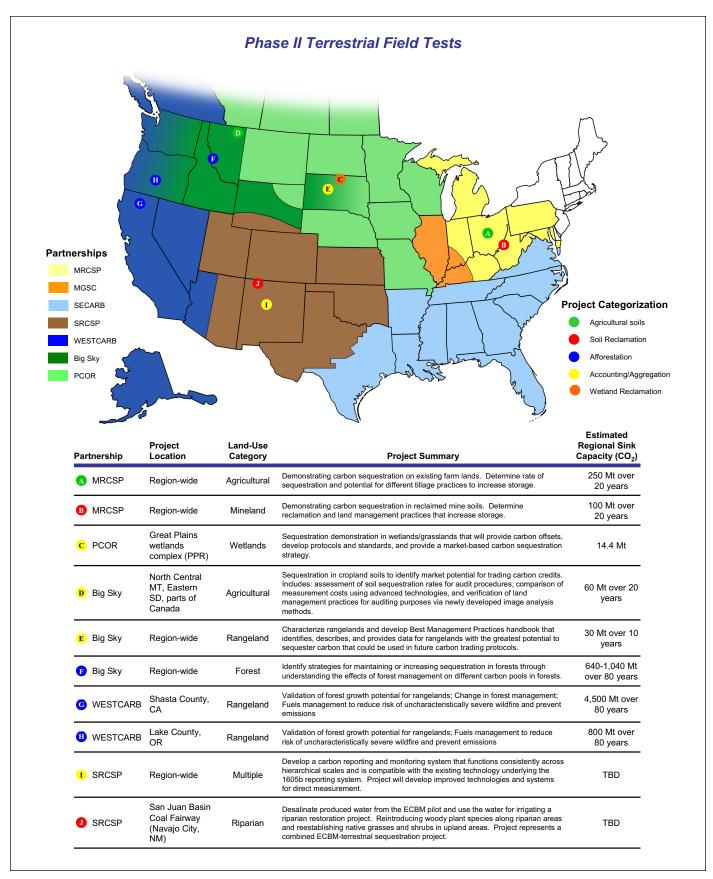


Figure 15. Regional Carbon Sequestration Partnerships

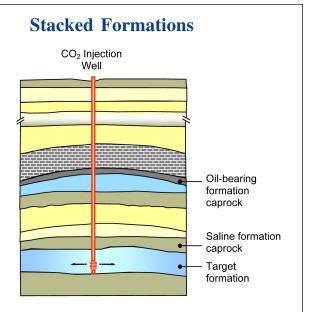
Table 7. Regional Partnership Outreach and Education Efforts

Partnership	Core Outreach	Unique Approach	
MRCSP		Intensified public outreach and education tailored to specific sites as field projects become visible (work closely with staff from host sites).	
MGSC	Interactive websites	Development of physical bench-scale models of CO ₂ storage to improve demonstrations at meetings.	
SECARB	 Presentations/Posters Fact sheets Workshops/symposia Stakeholder meetings Outreach articles Coordination with NATCARB NEPA/regulatory permitting requirements for public involvement 	• Fact sheets • Workshops/symposia • Stakeholder meetings • Outreach articles • Fact sheets develop effective message. Host mediated modeling workshops constituents. Develop and disseminate sequestration tutorials on CD	Conducted opinion research to identify stakeholder concerns in order to develop effective message.
SRCSP			Host mediated modeling workshops to facilitate learning among constituents. Develop and disseminate a library of interactive CO ₂ sequestration tutorials on CD.
WESTCARB		Support independent university research to obtain an objective assessment of public outreach activities.	
Big Sky		Establish the Energy Future Coalition, Annual Energy Forum, and State Legislative Symposia.	
PCOR		Plan to create four 30-minute videos produced by Prairie Public Television that describe in detail geologic sequestration, terrestrial sequestration, carbon trading markets, and sequestration and global warming.	

Deployment Phase (2009-2017)

As part of the Deployment Phase of the Regional Partnerships, DOE plans to include a number of large volume sequestration tests. These tests will be designed to address R&D issues associated with three major steps, namely (1) site selection and characterization; (2) operations and well closure; and (3) post-closure monitoring.

The projects in the Validation Phase are designed to demonstrate that regional sinks have the potential to store thousands of years' of CO₂ emissions in the U.S.. The large volume sequestration tests in the Deployment Phase will be conducted to address issues such as sustainable injectivity, well design for both integrity and increased capacity, and formation behavior with respect to prolonged injection. Issues such as these can only be addressed by scaling up sequestration projects' size and duration. These large scale tests will be an order of magnitude larger in size (up to 1,000,000 tons of CO₂) than tests conducted in the Validation Phase.



Researchers at the University of Texas Bureau of Economic Geology have pioneered a novel "stacked" approach to CO₂ storage field tests in saline formations. CO₂ is injected into a target formation that underlies a proven oil-bearing seal.

The oil-bearing cap rock serves as a second barrier against CO_2 migration to the surface and affords scientists an opportunity to learn about the fate and transport of CO_2 injected into a saline formation with negligible risk of adverse environmental consequences.

PROGRAM MANAGEMENT

The DOE is dedicated to achieving the Carbon Sequestration Program goals and to utilizing the Program funds as effectively as possible (Figure 16). This is achieved through cooperative and collaborative relationships, both domestically and internationally, competitive solicitations, analysis and project evaluation, project merit reviews, and proactive public outreach and education. These activities support and enhance the R&D being conducted in the laboratory and the field. Following are management highlights.

Public/Private Partnerships. Public/ private partnerships and cost-shared R&D are a critical part of technology development for carbon sequestration. These relationships draw on pertinent capabilities that the coal, electricity supply, oil and gas, refining, and chemical

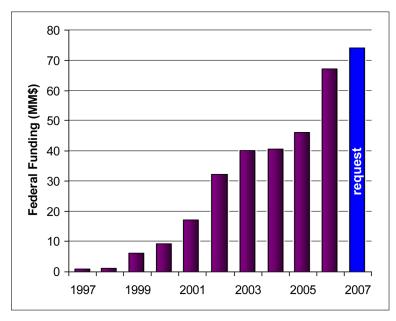


Figure 16. DOE Sequestration Program Budget

industries have built up over decades and the technical knowledge base shared with the National Laboratories, federal and state geological surveys, and academia. The program engages the research community through competitive solicitations, which bring forward the companies and researchers with the best ideas and strongest capabilities, and also challenges submitters to offer significant cost-share, leveraging Federal dollars.

In-House R&D at NETL. Three Focus Areas, including Energy System Dynamics, Geological and Environmental Sciences, and Computational and Basic Sciences at NETL conduct science-based research and analysis in areas related to carbon sequestration using in-house facilities and resources at NETL. The Focus Areas have been successful in fostering formal and information collaborative relationships with industry and academia in these high-risk research endeavors. The Focus Areas also provide FE/NETL with a scientific understanding of the underlying technologies and, thus, enhances its effectiveness in implementing the carbon sequestration R&D portfolio.

Interagency Coordination. In each sequestration area, the DOE program collaborates with other agencies with overlapping responsibilities. For example, during 2003 and 2004 the DOE Carbon Sequestration Program collaborated with the National Academy of Sciences (NAS) in an effort to bolster R&D efforts in Breakthrough Concepts. A workshop hosted by DOE and the National Research Council (NRC) identified priorities for breakthrough research and a solicitation drawing from the research results produced a pool of over one hundred proposals. Eight awards were made in March 2004 and the work is proceeding. The information from the workshop was used in a funding opportunity announcement (FOA) on capture technology that was released in FY06.

International Collaboration. The international Carbon Sequestration Leadership Forum (CSLF) is a voluntary climate initiative of developed and developing nations. Members engage in cooperative technology development aimed at enabling the early reduction and steady elimination of carbon dioxide emissions from electric generation and other heavy industry activities. The CSLF has endorsed seventeen carbon sequestration projects around the world. Information on the CSLF and its activities can be found at http://www.cslforum.org

Systems, Economic, and Benefits Analyses. Systems analyses and economic modeling of potential new processes are crucial to providing sound guidance to R&D efforts, which are investigating a wide range of CO₂ capture options. Many of the technologies being developed by the program are investigated at the laboratory or pilot scale. Systems analyses offer the opportunity to visualize how these new technologies might fit in a full-scale power plant and identify potential issues with their integration. Results of the analyses help make decisions on what technologies the Program should continue funding and how the research can be modified to help the technology succeed at full scale.

Systems analysis efforts are aided through the use of modeling tools. To enable the modeling of sequestration systems, NETL funds the development of the Integrated Environmental Control Model (IECM) which is a publicly-available model that now includes options for CO₂ capture and storage. http://www.iecm-online.com/

The Program conducts independent studies and participates in cross-cutting studies to model the future national energy situation. These activities include Program-specific analyses to consider how sequestration might help meet future CO₂ emissions reductions goals. They also include broader efforts that use large models like DOE's National Energy Modeling System (NEMS) or ICF's Integrated Planning Model (IPM) to address the benefits and roles of the full suite of advanced fossil energy technologies. The most recent programmatic benefits analysis can be downloaded at: http://www.netl.doe.gov/publications/carbon_seq/refshelf.html

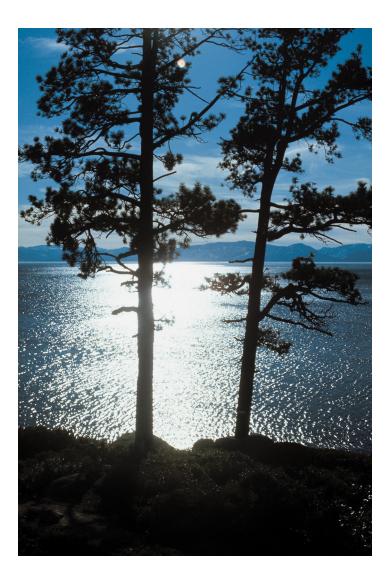
Education and Outreach. The notion of capturing and sequestering carbon dioxide and other greenhouse gases is relatively new, and many people are unaware of its role as a greenhouse gas reduction strategy. Increased education and awareness are needed to achieve acceptance of carbon sequestration by the general public, regulatory agencies, policy makers, and industry. This will enable future commercial deployments of advanced carbon sequestration technology. The following activities highlight the Program's education and outreach efforts:

- Carbon Sequestration Webpage at the NETL site
- Carbon Sequestration Technology Roadmap and Program Plan revised annually
- Carbon Sequestration Newsletter distributed monthly
- Middle School and High School Educational Curriculums on GHG Mitigation Options disseminated through workshops at the National Science Teacher Association Conferences
- Carbon Offsets Opportunity Program Website
- Carbon Sequestration Project Development Guide scheduled for release in FY2007
- Carbon Sequestration Handbook scheduled for release in FY2006
- The National Conference on Carbon Sequestration, held annually in the late spring in the Washington, DC, area.

In addition, the program management team participates in technical conferences through presentations, panel discussions, breakout groups, and other formal and informal venues. These efforts expose professionals working in other fields to the technology challenges of sequestration and also enable examination of some of the more detailed issues underlying the technology.

In concert with R&D, the Program seeks to engage non-governmental organizations (NGOs) and federal, state, and local environmental regulators to raise awareness of the priority the Program places on evaluating the potential environmental impacts of sequestration and ensuring that selected technologies preserve human and ecosystem health. Many of the Program's R&D projects have their own outreach component. For example, the Regional Partnerships will enhance technology development but also engage regulators, policy makers, and interested citizens at the state and local level through innovative outreach mechanisms. In addition, the Regional Partnerships will implement action plans for public education in the form of mailing lists, public meetings, media advertising, local interviews and education programs available at libraries, schools, and local businesses.

The Program works directly with NGOs and the environmental community through a variety of activities. Successful outreach entails two-way communication, and the Program will address concerns voiced at outreach venues and continually assess the adequacy and focus of the current R&D portfolio.



Carbon Sequestration-Related Web Pages

NETL	National Energy Technology Laboratory http://www.netl.doe.gov/sequestration
A CONTRACTOR OF THE PARTY OF TH	U.S. Department of Energy, Office of Fossil Energy http://www.doe.gov/sciencetech/carbonsequestration.htm
carbon sequestration leadership forum	Carbon Sequestration Leadership Forum http://www.cslforum.org/
West Coast Regional Carbon Sequestration Partnership westcarb.org	West Coast Regional Partnership http://www.westcarb.org/
Southwest Regional Partnership on Carbon Sequestration	Southwest Regional Partnership http://www.southwestcarbonpartnership.org/
BIGSKYCARBON SEQUESTRATION PARTNERSHIP	Big Sky Partnership http://www.bigskyco2.org/
The Plains CO ₂ Reduction Partnership	Plains CO ₂ Reduction Partnership http://www.undeerc.org/pcor/
MGSC	Midwest Geological sequestration Consortium http://www.sequestration.org/
MRCSP MIDWEST REGIONAL CARBON SEQUESTRATION PARTNERSHIP	Midwest Regional Carbon Sequestration Partnership http://l98.87.0.58/default.aspx
Southeast Regional Carbon Sequestration Partnership	Southeast Regional Carbon Sequestration Partnership http://www.secarbon.org/

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U.S. Department of Energy Office of Fossil Energy

Printed in the United States on recycled paper



